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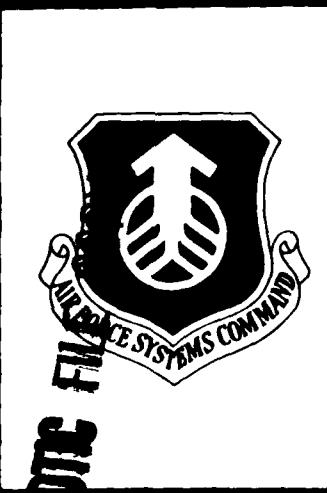
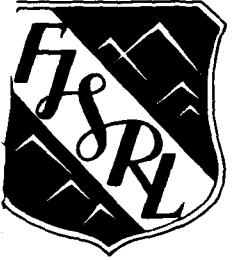
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APRIL 1981

**THERMOCHEMICAL DECOMPOSITION
OF TNT: RADICAL IDENTIFICATION
AND THEORETICAL STUDIES**

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PROJECT 2303

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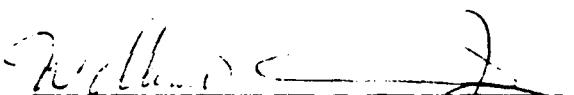
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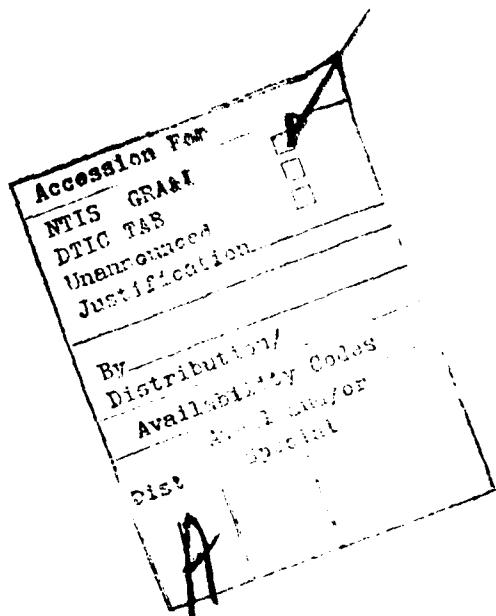
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TNT, is likely. Comparisons of the theoretical activation energy and the deuterium kinetic isotope effect for this step are in excellent agreement with measured values for these quantities early in the TNT decomposition. The nitro group removal is apparently facilitated by interaction with a second molecule in the system (HMB in the binary system or another TNT in the pure TNT system), which weakens the C-NO₂ bond either by transferring a hydrogen atom or forming a charge-transfer complex. Other potential first steps in the mechanism have been investigated theoretically.



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THERMOCHEMICAL DECOMPOSITION OF TNT:

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APRIL 1981

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PREFACE

The research described here was performed largely under Project 2303-F3-05 (Chemical Structure/Bonding Decomposition Relationships) and Project 2303-F4-03 (Molecular Orbital Calculations of Excited Species). A portion of the funding was provided by the AF Armament Laboratory under Project Order ATL-1-68. Mr. Thomas Floyd was the AFATL Program Manager.

TABLE OF CONTENTS

	<u>PAGE</u>
Preface	i
List of Figures	iii
Introduction	1
Experimental	1
Results and Discussion.	2
Radical Identification.	2
MNDO Calculations	6
Conclusions	15
References	18
Abbreviations, Acronyms, and Symbols	20

LIST OF FIGURES

<u>FIGURE</u>		<u>PAGE</u>
1	Early TNT Radical Spectra	3
2	Late TNT Radical Spectra	5
3	Early TNB Radical Spectra	7
4	Transition State for Intramolecular Hydrogen Transfer	13
5	Transition State for Intermolecular Oxygen Insertion	13
6	Transition State for Nitro-Nitrite Rearrangement	16

LIST OF TABLES

I	Results of MNDO Calculations: Reaction ΔH° 's . .	11
II	Results of MNDO Calculations: Activation Energies and Deuterium Isotope Effects . . .	15

INTRODUCTION

The thermochemical decomposition of 2,4,6-trinitrotoluene (TNT) and related nitroaromatics in the liquid phase has been studied by a variety of techniques for many years¹⁻¹⁷. Janzen first observed radical formation during the thermochemical decomposition of nitroaromatics with electron paramagnetic resonance (EPR) techniques¹⁸. We have studied the thermal decomposition kinetics of TNT by EPR¹⁷. This paper compares EPR studies of the initial TNT radicals with MNDO molecular orbital calculations¹⁹⁻²² on TNT and model systems to identify the initial radicals produced and propose plausible first steps in the thermal decomposition of TNT.

EXPERIMENTAL

EPR spectra were recorded on a Varian E-109 spectrometer operating in the X-band using a standard TE₁₀₂ rectangular cavity as previously described²⁶. A custom-built variable temperature apparatus utilizing a Scanlon Co. heater maintained temperatures in the cavity to $\pm 1^{\circ}\text{C}$ as measured by a Doric trendicator. TNT²⁴ and trinitrobenzene (TNB)²⁵ were synthesized using previously described procedures. Hexamethylbenzene (HMB) was purchased from the Aldrich Chemical Co. All compounds were purified by recrystallization from ethanol prior to use. Mixtures of compounds were prepared for EPR analysis by mixing the components in the molten state in quartz EPR tubes at temperatures below 170°C.

Simulation of EPR spectra for comparison with the experimental spectra was accomplished with a program written and generously provided by Dr. Ira Goldberg of Rockwell Science Center. This program is capable of simulating overlapping spectra from multiple radicals.

The MNDO and MINDO/3 molecular orbital programs were used to calculate heats of formation and geometries of all suspected intermediates and transition states for mechanisms tested. A related force constant program, also developed by M. J. S. Dewar, *et. al.*, was used to examine suspected transition states and provide vibrational frequencies in order to calculate thermodynamic quantities. Deuterium kinetic isotope effects for some steps also were calculated using these thermodynamic quantities.

RESULTS AND DISCUSSION

RADICAL IDENTIFICATION:

Previously we observed at least two radicals from the thermochemical decomposition of pure molten TNT¹⁷. The final, or product, radical has been tentatively identified as a polymeric radical whose number of radical sites grows at an exponential rate throughout the decomposition. The initial radical, whose spectrum is composed of at least twenty lines, has eluded identification until now. By careful comparison in the wings of the spectrum of pure TNT with spectra generated by doping the TNT with a small amount of HMB, we find that the TNT spectrum is consistent with the radical structure below:

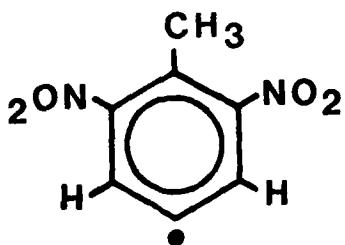


Figure 1 shows a comparison of the spectra of the radical formed early in the decomposition of pure TNT at 245°C and a mixture of TNT and HMB (14:1 w:w) at 200°C. The spectrum exhibited by the HMB-doped TNT sample

EARLY TNT RADICAL SPECTRA

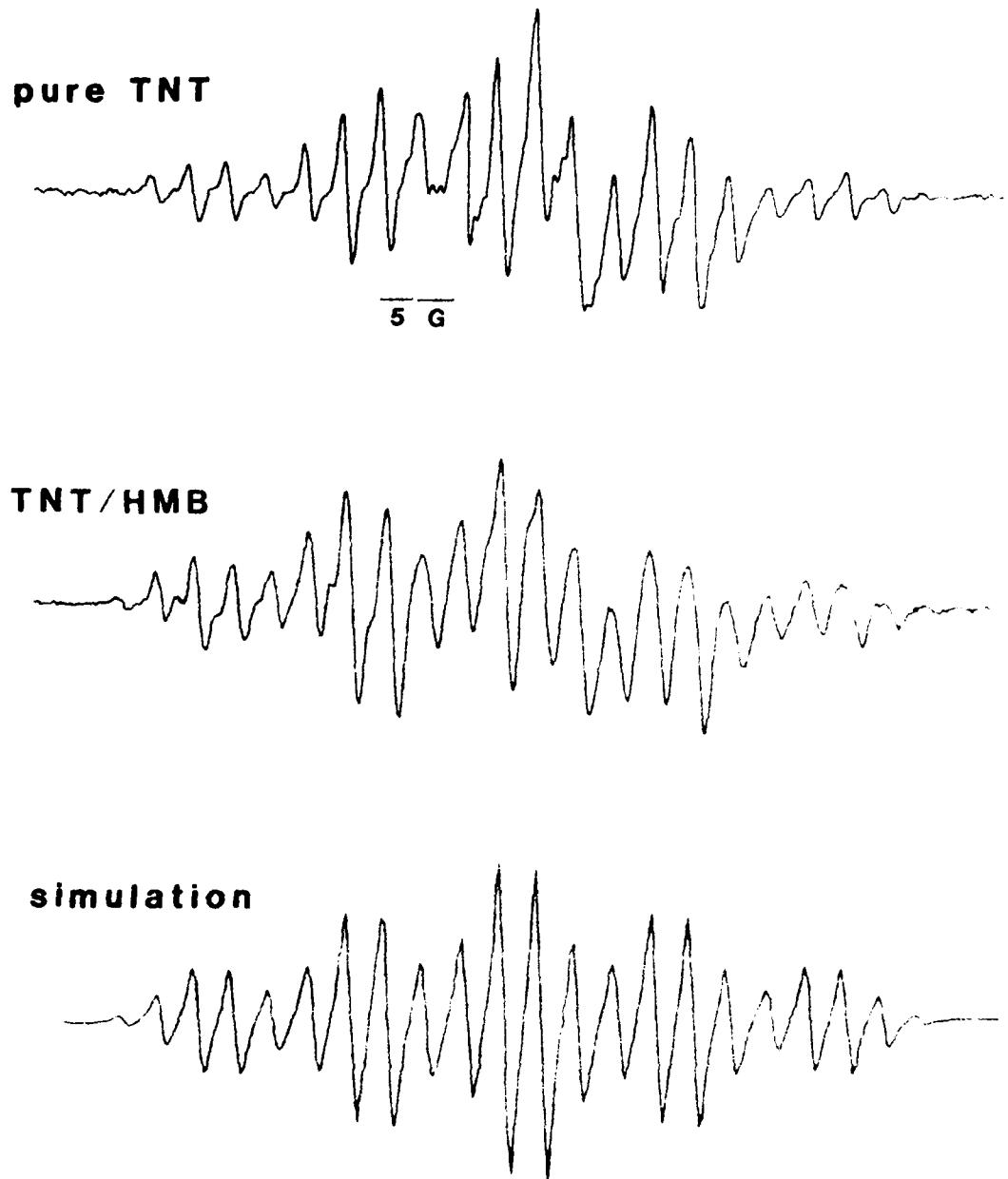


Figure 1

exhibits a large coupling constant of 10.3 G with an overall intensity pattern of 1:2:3:2:1, indicative of two equivalent nitrogens. Within each of these five groups, a six-line pattern is evident (coupling constant = 2.7 G) with intensity ratios of 1:5:10:10:5:1, indicative of five equivalent hydrogens. The computer simulated spectrum in Figure 1 using the measured couplings from the TNT/HMB spectrum shows a good match when two equivalent nitrogens and 5 equivalent hydrogens are assumed. The spectrum matches that of the initial radical from pure TNT decomposition in the wings. The simplest interpretation is that the five original hydrogens present in the TNT molecule are preserved in the radical, and one nitre group has been removed leaving two equivalent nitrogens. The apparent equivalence of the ring and methyl hydrogens has been noted for other radicals formed from TNT, in particular the radical anion²³. It is also interesting to note that the HMB-doped sample produces the initial radical spectra at much lower temperatures than pure TNT (~200°C instead of 245°C) and the spectrum remains practically unchanged for over thirty minutes at 200°C.

The center portion of the neat TNT radical spectrum is not identical with the HMB-doped TNT spectrum, even though the wings are. Simulations which include a single line polymer radical spectrum with the HMB-doped TNT spectrum can be made identical with the neat TNT spectrum by varying the relative amounts of the two radicals (polymer + TNT radical), as shown in Figure 2. The neat TNT spectrum is thus apparently the superposition of the polymer radical spectrum on that of the TNT radical identified in the HMB-doped experiments.

A reaction analogous to the HMB-doped TNT decomposition apparently occurs during the thermal decomposition of 1,3,5-trinitrobenzene (TNB)

LATE TNT RADICAL SPECTRUM

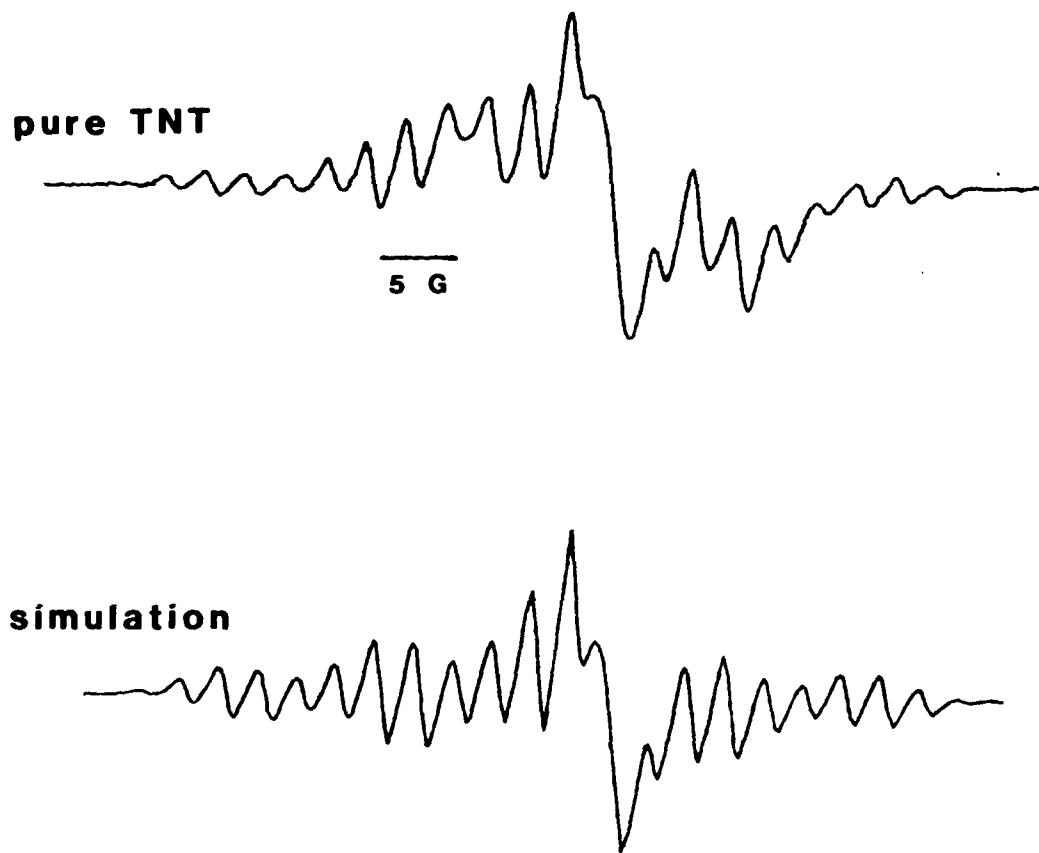
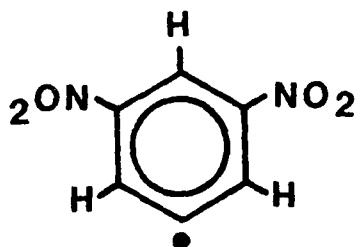


Figure 2

doped with a small amount of HMB. TNB is thought to be very stable at temperatures at which TNT decomposes rapidly (<250°C). However, the HMB-doped TNB (TNB: HMB 82:78 w/w) produces a strong radical signal at 200°C which is quite stable as shown in Figure 3. An overall five-line pattern (coupling constant = 10.7 G) with a 1:2:3:2:1 intensity pattern again indicates two equivalent nitrogens. Within each of the five groups is a four-line pattern (coupling constant = 2.6 G) with intensity ratios of 1:3:3:1, indicative of three equivalent hydrogens. A simulation based on these values shows good agreement. Thus TNB doped with HMB appears to form a radical analogous to the TNT radical with HMB:



MNDO CALCULATIONS:

Molecular orbital calculations using the MNDO and MNDO/3 methods developed by Dewar, et al.,¹⁹⁻²² have been carried out in this laboratory for the last several years. These methods have been shown to be useful in a variety of systems in the determination of plausible reaction mechanisms and kinetic parameters. We have applied these methods to the study of the initial steps of TNT and related nitroaromatics thermochemical decomposition. Calculated results for the activation energies and deuterium kinetic isotope effects of suspected mechanistic steps are compared with these experimentally-determined quantities using IDSC and EPR

EARLY TNB RADICAL SPECTRUM

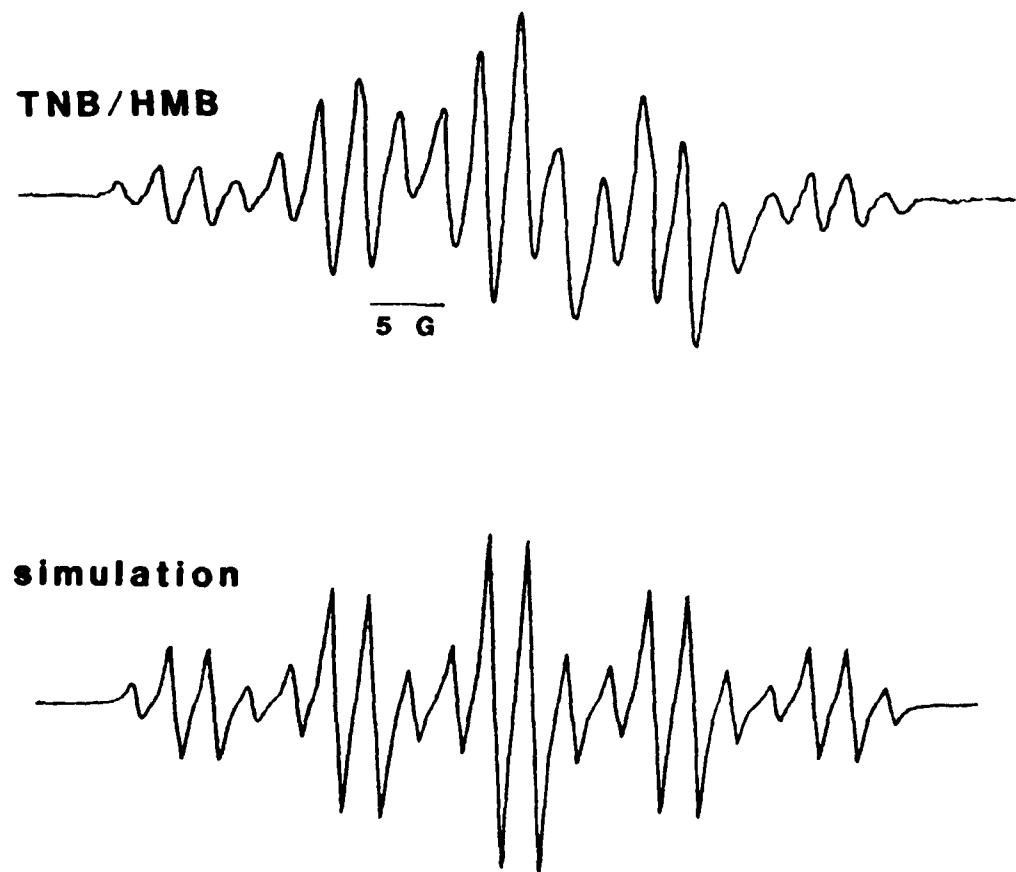
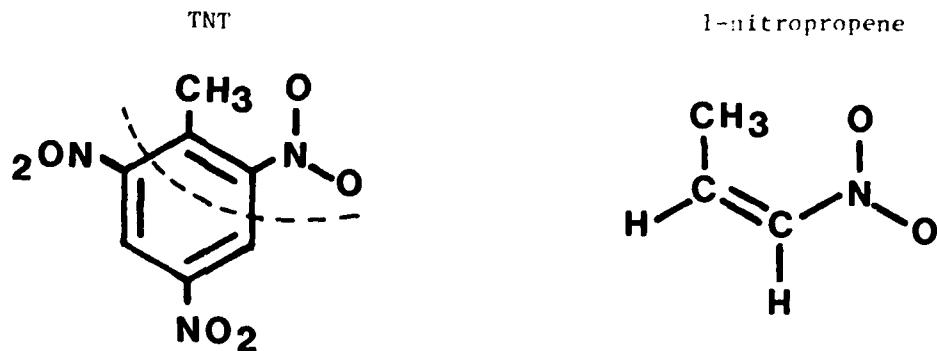


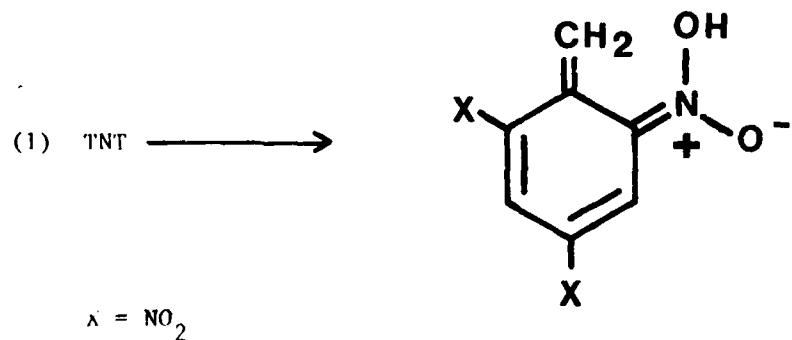
Figure 3

techniques. Also, structures of possible intermediates are compared with experimental spectra.

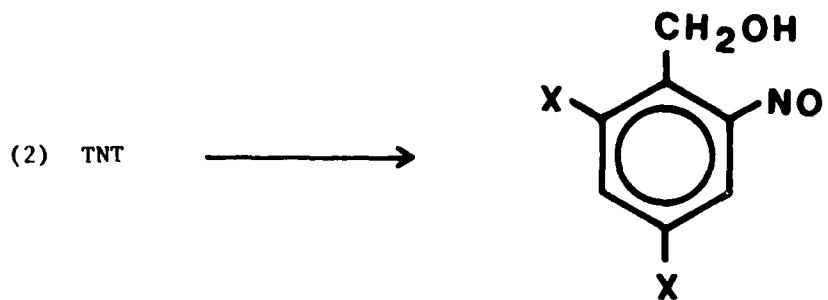
Because of the large amounts of computer time to completely optimize the geometries of the TNT species involved in suspected decomposition steps, we chose to use 1-nitropropene as a model system:



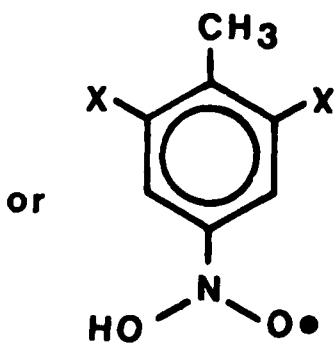
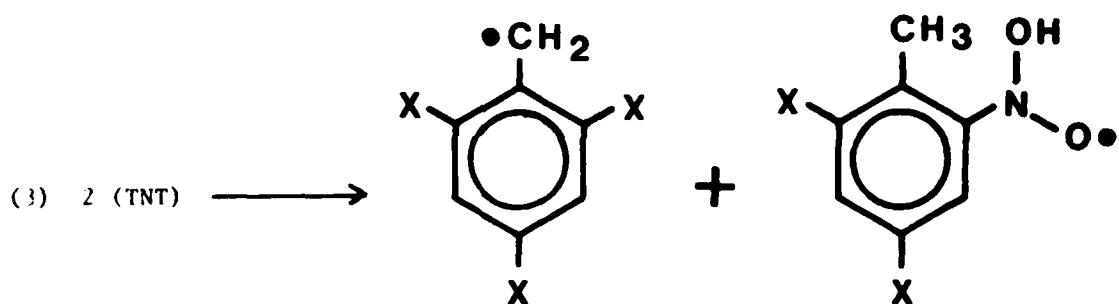
Previous experimental evidence¹⁵ had indicated involvement of a methyl group-hydrogen in the rate-determining step. Based on this, six potential rate-determining steps were selected for calculations of ΔH° and E_a :



Intramolecular H Transfer

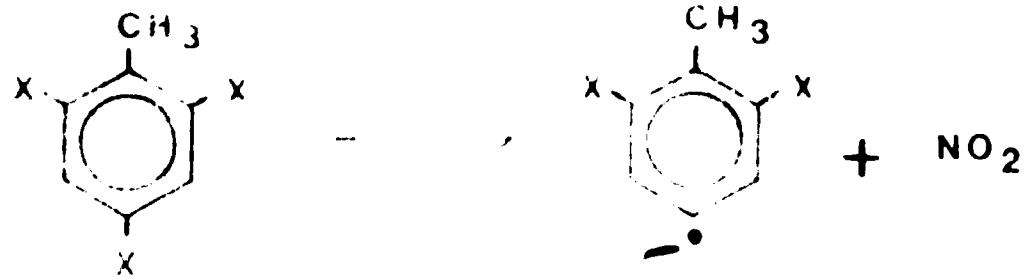
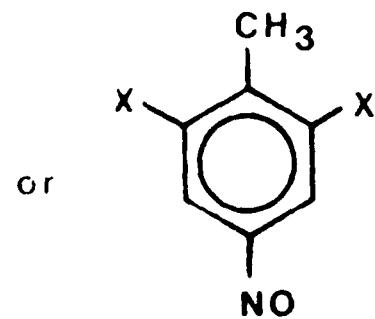
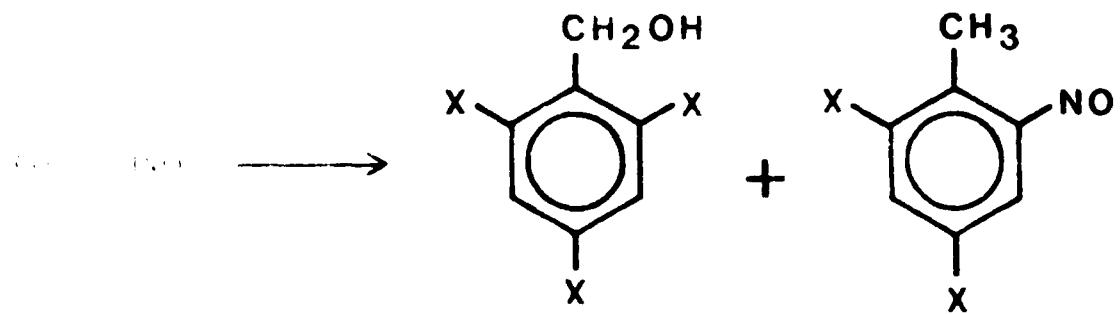


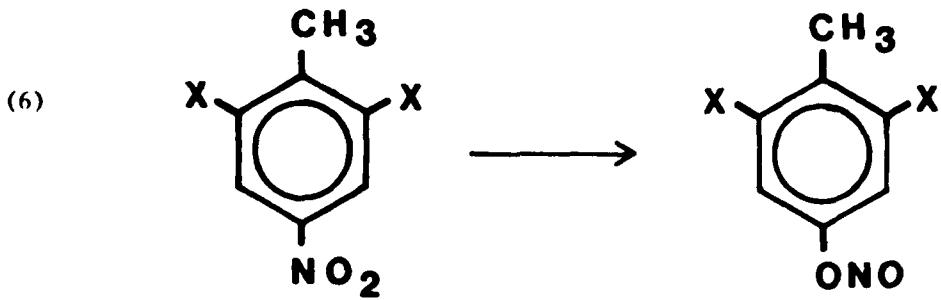
Intramolecular O Insertion



$X = \text{NO}_2$

Intermolecular H Transfer





Step (5) is a removal of an NO_2 group (either para or ortho). Step (6) is a nitro group rearrangement to form a nitrite species.

In order to test the usefulness of the 1-nitropopene model in simulating TNT behavior, ΔH° 's for all six steps were calculated for both TNT and the 1-nitropopene model system, all geometries being optimized. The results in Table I are MNDO results. MNDO/3 results gave the same agreement between the two molecular systems that the MNDO results did.

TABLE I
Results of MNDO Calculations: Reaction ΔH° 's

<u>Step</u>	<u>ΔH° (TNT System) (Kcal/mole)</u>	<u>ΔH° (1-nitropopene system) (Kcal/mole)</u>
(1) Intramolecular H Transfer	+16.6	+14.5
(2) Intramolecular O Insertion	-49.9	-49.3
(3) Intermolecular H Transfer	+16.8	+19.5
(4) Intermolecular O Insertion	-52.4	-48.5
(5) NO_2 Removal	+32.3	{+26.9 (ortho- NO_2) +32.5 (para- NO_2)}
(6) Nitro Rearrangement	-38.4	-41.1 (para- NO_2)

Thus it appears that the nitropropene system is at least a potential model for simulating TNT decomposition steps. It is a good model if the calculated activation energies are also similar.

We simulated the reaction pathway for each of the six steps by defining a reaction coordinate, fixing it at various intermediate points along the pathway, and then allowing all other geometric variables to optimize at each value of the reaction coordinate. If a maximum was located along the pathway, the transition state optimization program was run. Finally, the vibrational force constant program was employed on the transition state geometry to support the existence of a transition state by the presence of one negative vibrational force constant, which is identified as the reaction coordinate. Each of the six steps will be discussed in turn.

The intramolecular hydrogen transfer (1) calculations for 1-nitropropene produced a species which proved to be a transition state with an activation energy of 63.8 kcal/mole. The most recently measured value (EPR) for the activation is 40.9 kcal/mole¹⁷. The optimized geometry from the calculations was intermediate between that of the reactant and product, with the O-H bond order being 0.48 and the C-H bond order 0.39. The geometry is shown in Figure 4. A calculation of a deuterium kinetic isotope effect utilizing the calculated force constants and moments of inertia yielded a k_H/k_D value of 2.2 at 227°C. The measured value of k_H/k_D for the rate-determining step of TNT decomposition near this same temperature is 1.¹⁵ Thus the calculations do not rule out this intramolecular hydrogen transfer as the rate-determining step for TNT thermochemical decomposition, particularly since MNDO usually overestimates activation energies for hydrogen transfer reactions.

**TRANSITION STATE FOR INTRAMOLECULAR
HYDROGEN TRANSFER**

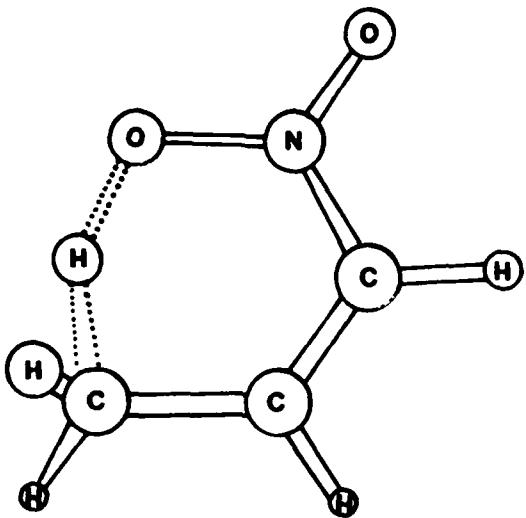


Figure 4

**TRANSITION STATE FOR INTERMOLECULAR
OXYGEN INSERTION**

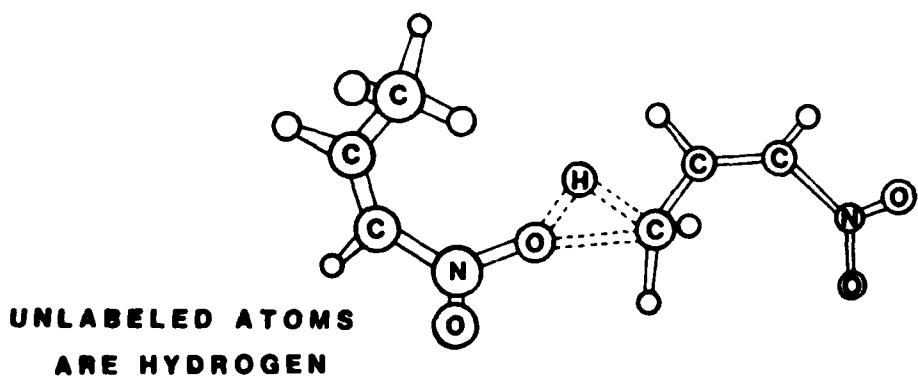


Figure 5

On the other hand, the intramolecular oxygen insertion (2) calculations for 1-nitropropene gave very high energy barriers even though ΔH° for this step is quite negative. In one case for which the methyl group was not allowed to rotate while the oxygen was moved toward the carbon, the molecule dissociated into acetylene and methyl nitrite with an activation energy of 96 kcal/mole. If complete relaxation of the methyl group was allowed, no stable product was formed. Thus it appears that this step is not likely during the thermochemical decomposition of TNT.

The intermolecular hydrogen transfer (3) transition state has not yet been located, but approximations point to an activation energy of 82 kcal/mole. This step also appears to have too high an activation energy to be a viable candidate for the first step of TNT decomposition.

The intermolecular oxygen insertion reaction (4) produced a transition state with an activation energy of 110 kcal/mole. The geometry of this transition state is shown in Figure 5.

We also investigated rearrangement of an NO_2 group and removal of an NO_2 group from the molecule, even though these steps would not produce a primary deuterium kinetic isotope effect as indicated by the previous experimental evidence¹⁵. We found that the calculated dissociation energy for 1-nitropropene of 32.3 kcal/mole agreed well with the experimental value for the activation energy, particularly since MNDO typically underestimates C- NO_2 bond energies. In addition, the calculated deuterium kinetic isotope effect at 227°C for NO_2 removal was 1.7, even though it is a secondary kinetic isotope effect. This, too, agrees well with the experimental value of approximately 1.7. The nitro group rearrangement to nitrite for 1-nitropropene had a calculated activation energy of 52.4 kcal/mole,

slightly more than the experimental number for TNT. The geometry of the transition state is shown in Figure 6. This step cannot be ruled out as a potential first step. In addition, if NO then dissociates from the molecule, the resulting radical, with an oxygen on the para position, could give qualitatively the experimentally observed EPR spectrum.

Table II summarizes activation energies and deuterium kinetic isotope effects for both 1-nitropropene and TNT. The activation energy given for TNT for the intramolecular hydrogen transfer step is a lower bound, and the one for the intermolecular hydrogen transfer is an upper bound.

TABLE II
RESULTS OF MNDO CALCULATIONS:

ACTIVATION ENERGIES (KCAL/MOLE) AND DEUTERIUM ISOTOPE EFFECTS

PROCESS	E_a (1-NP)	E_a (TNT)	K_H/K_D (1-NP)
(1) Intramolecular H Transfer	63.8	>55	2.2
(2) Intramolecular O Insertion	96	—	—
(3) NO_2 Removal	32.3	{ 26.9(o- NO_2) 32.5(p- NO_2)	1.7
(4) Nitro Rearrangement	52.4	—	—
(5) Intermolecular H Transfer	~82	<122	—
(6) Intermolecular O Insertion	110	—	—

CONCLUSIONS

An initial radical in the thermochemical decomposition of TNT and related nitroaromatics is one in which a nitro group or an NO group has been removed from the TNT molecule. MO calculations for removal of a nitro group from the molecule are consistent with experimental evidence

**TRANSITION STATE FOR
NITRO-NITRITE REARRANGEMENT**

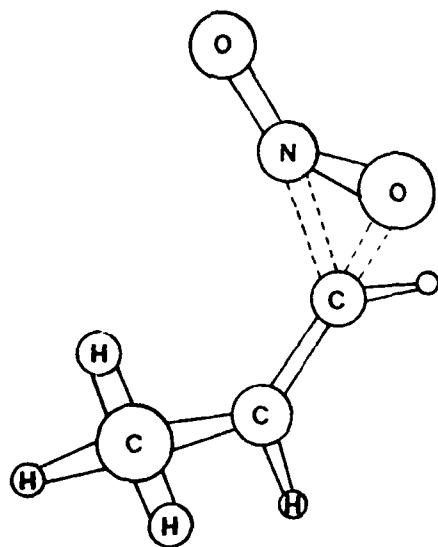


Figure 6

both for the activation energy and the deuterium kinetic isotope effect.

The enhancement of radical production upon addition of HMB indicates that the interaction of a second species results in much easier NO₂ removal.

Two likely mechanisms arise:

(1) The donor species (HMB) transfers a hydrogen atom to the acceptor species (TNT or TNB). The removal of HONO can then be possibly accomplished more easily than the original nitro group.

(2) A charge-transfer complex (HMB/TNT or HMB/TNB) is formed which weakens in some manner the C-nitro group bond. Thus NO₂ can be removed more easily.

The calculations indicate that oxygen atom insertions are unlikely due to the high energies of the transition states involved. Also, the activation energy for intermolecular hydrogen transfer has a value which is probably inconsistent with the experimental value. Intramolecular hydrogen transfer or nitro group rearrangement to the nitrite cannot be ruled out as the initial step, although they appear to be less likely than simple nitro group removal.

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ABBREVIATIONS, ACRONYMS, AND SYMBOLS

TNT - 2,4,6 Trinitrotoluene

EPR - Electron Paramagnetic Resonance

MNDO - Modified Neglect of Diatomic Overlap

MINDO/3 - Modified Intermediate Neglect of Differential Overlap/3

TE₁₀₂ - Transverse Electric Mode 102

TNB - 1,3,5 Trinitrobenzene

HMB - Hexamethylbenzene

G - Gauss

w:w - Weight to Weight Ratio

°C - Degrees Centigrade

ΔH° - Change of enthalpy for the reaction

E_a - Activation energy for the reaction

IDSC - Isothermal Differential Scanning Calorimeter

X - Nitro group

K_H/K_D - Deuterium Kinetic isotope effect

